



Microwave-treated graphite felt as the positive electrode for all-vanadium redox flow battery



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HIGHLIGHTS

- Graphite felt treated by microwave method works as positive electrode of VRFB firstly.
- The microwave-treated graphite felt carries more hydrophilic groups on its defects.
- Graphite felt treated via microwave exhibits excellent electrochemical activity.
- The single cell performance is improved remarkably with the use of modified electrode.

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ABSTRACT

An environmental, economic, and highly effective method based on microwave treatment was firstly used to improve the electrochemical activity of graphite felt as the positive electrode in all vanadium redox flow battery (VRFB). The graphite felt was treated by microwave and characterized by Fourier transform infrared and scanning electron microscopy. The electrochemical performance of the prepared electrode was evaluated with cyclic voltammetry and electrochemical impedance spectroscopy. Results show that graphite felt treated by microwave for 15 min at 400 °C exhibits excellent electro-catalytic activity and reactive velocity to vanadium redox couples. The coulombic, voltage, and energy efficiency of the VRFB with as-prepared electrodes at 50 mA cm⁻² are 96.9%, 75.5%, and 73.2%, respectively; these values are much higher than those of cell-assembled conventionally and thermally treated graphite felt electrodes. The microwave-treated graphite felt will carry more hydrophilic groups, such as –OH, on its defects, and rough degree of the surface which should be advantageous in facilitating the redox reaction of vanadium ions, leading to the efficient operation of a vanadium redox flow battery. Moreover, microwave treatment can be easily scaled up to treat graphite felt for VRFB in large quantities.

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1. Introduction

Redox energy storage systems proposed by Sum et al. [1] have unique advanced characteristics, namely, low operation and maintenance costs, long lifecycle, deep-discharge capability, flexible design, high reliability, and efficient generation of electricity [2–4]. In particular, the all-vanadium redox flow battery (VRFB) is a promising candidate for storing electrical energy. VRFB offers the advantage of low contamination of metal cations by employing the same element in both electrolytes [5]. VRFBs have been significantly improved, but these improvements are

insufficient for VRFBs to replace the current internal combustion engines. Therefore, the energy efficiency (EE) of VRFBs must be improved prior to commercialization. The EE of a VRFB depends largely on the physicochemical properties of its electrodes, because the electrochemical reactions of vanadium ions occur on the electrode surface [6,7]. In VRFB, carbon-based materials are widely used in the electrodes to catalyze reactions [8–11]. Graphite felt with a large surface area is an appropriate material, because it provides abundant redox reaction sites and maintains good electronic conduction and mechanical stability during cycles. A typical electrode material for VRFB is graphite felt, which exhibits good stability in highly acidic solutions and provides a large reactive surface area for a sufficient number of redox reaction sites [12]. However, graphite felts must be subjected to surface treatments before being utilized as electrodes to ensure that

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their electrochemical activity and wettability originated from a hydrophobic surface [13,14].

In the past, much attention has been paid to the improvement of the electrochemical properties of graphite felt electrodes. Considerable studies about the modification of electrode materials have been carried out to enhance their electrochemical performance; those methods include electrochemical oxidation [15], thermal activation [16,17], acid treatment [18,19], nitrogen modified [20], and metal modified [21,22]. An effective way to achieve enhanced electrochemical performance is by the thermal treatment of graphite felts to increase the surface functional groups of C–O and C=O dramatically, particularly C–OH that was expected to electrochemically catalyze the electrode reaction [23,24]. B. Sun and M. Skyllas Kazacos [16] also showed that graphite felt thermally heated at 400 °C exhibited the greatest improvement in terms of the performance of the vanadium cell.

Much attention has been paid to the surface hydroxylated function of carbon material [25–27]. However, the conventional thermal treatment for graphite felt electrodes is known to be energy or time-consuming or harmful to the environment.

Microwave efficiently heats the preform from the inner part to the surface and produces an inverted temperature gradient because of the convective and radiative heat loss on surface [28,29]. Meanwhile, microwave has the advantage of rapid heating and low energy consumption. In general, carbon materials are good absorbent of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties to be used as microwave receptors [30]. Previous work has demonstrated that activated carbons from different carbon sources can be prepared by microwave-assisted heat treatment [31,32], which proves that microwave heating is better than conventional methods of heat treatment because of certain advantages, such as high heating rate, easy control of the heating process, and no direct contact between the heating source and the materials [33]. The temperature of the reaction system is homogeneous to the process because of the penetrability of microwave [34]. Menéndez et al. claimed that carbon materials are generally a good absorbent of microwaves, i.e., they are easily heated by microwave radiation [30].

Thus, we proposed using microwave-treatment to improve the electrochemical activity of graphite felt electrodes in VRFB at 400 °C. In our research, the positive electrode for VRFB was mainly studied. In order to eliminate the influence of the negative electrode on cell potential, we used the graphite felt treated by microwave as the positive electrode and used the hydrogen electrode and H₂ to replace the graphite felt and V²⁺/V³⁺ couple in the negative electrode in the VRFB performance test.

2. Experimental

2.1. Preparation and characterization of microwave-treated graphite felt

2.1.1. Preparation of microwave-treated graphite felt

Commercial graphite felt was used particularly for this study (3 mm thickness PAN-based graphite felt, <16 mΩ cm², Hongwei Co., Gansu). The graphite felt was microwave treated with a NJZ4-3A microwave sintering oven (Jiequan Microwave Development Co., Ltd., Nanjing) which contains an infrared temperature measuring instrument to measure the temperature of the samples and then with a different microwave program. The graphite felt was put in a silicon carbide crucible and placed inside another larger silicon carbide crucible, which was stuffed with

glass wool. Glass wool is mainly used to avoid breaking and cracking the quartz turntable in the microwave sintering oven by minimizing the heat transfer to the turntable. The whole assembly was kept at the center of the turntable. At 400 °C under atmospheric conditions, the graphite felt was homogeneously exposed to microwave radiation for various exposure times, i.e., 10 min, 15 min, and 20 min and designated as graphite felt-10 min, graphite felt-15 min, and graphite felt-20 min, respectively.

Another graphite felt, which was heated by conventional thermal treatment in a muffle oven at a constant temperature of 400 °C for 30 h, was prepared for comparison (referred to as graphite felt-30 h) as described in Ref. [16].

2.1.2. Characterization of microwave-treated graphite felt

2.1.2.1. SEM for microwave-treated graphite felt. The morphology of the materials was analyzed with a JSM-6360LV microscope (JEOL, Japan) at an accelerating voltage of 20 kV. The microscope was also utilized to examine the appearance of the microwave-treated graphite felt at 20 kV and the magnification of 15,000.

2.1.2.2. FT-IR for microwave-treated graphite felt. The Fourier transform infrared (FT-IR) spectra of the samples were recorded in an FT-IR spectrometer (FTIR430, Jasco Co., Japan). First, graphite felts were milled to be powder. Second, 1 mg of the powder was mixed with 50 mg of KBr. The mixture was pressed to form disks as the determinant.

2.1.2.3. Cyclic voltammetry and electrochemical impedance spectroscopy for microwave-treated graphite felt. The electrochemical activity of the as-prepared electrodes was evaluated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS results were obtained in the electrochemical workstation, Autolab PGSTAT302N, (Ecochemie Co., Netherlands) in 0.5 M VOSO₄ + 3 M H₂SO₄ solutions at room temperature. A three-electrode system was utilized in the electrochemical test with microwave-treated graphite felt as the working electrode; saturated calomel electrode (SCE) and Pt foil were employed as the reference and counter electrode, respectively. Salt bridge with Rudin capillary was used to connect the reference and working electrodes. The scanning range of CV was limited from 0 V to 1.6 V (vs. SCE), and the scanning rate was 2 mV s⁻¹. Impedance spectra were obtained by sweeping various frequencies in the range of 10⁻² Hz to 10⁵ Hz. The potential was fixed at 0.79 V in all EIS measurements to ensure similar polarization.

2.2. Single cell evaluation

Constant current charge–discharge tests were performed with a single cell and CT2001D LAND battery test system (LAND Electronics Co., Wuhan). A piece of microwave-treated graphite felt with an active area of 12 cm² (3.0 cm × 4.0 cm) was used as a positive electrode. Nafion 212 ion exchange membrane was utilized as the separator. A graphite plate with a serpentine flow field on its surface served as the current collector. The cell was sealed with rubber washers. The initial positive electrolyte was 100 mL 0.5 M V (IV) + 1 M H₂SO₄ solution, which was stored in tanks outside the cell. The electrolytes were pumped into the compartments as flowing liquid during cell operation. The upper limit and lower limit of discharge voltage were 1.7 V and 0.8 V, respectively. The hydrogen electrode and H₂ replaced the graphite felt and V²⁺/V³⁺ couple in the negative side. Another single cell with graphite felt-30 h as a positive electrode was prepared for comparison.

3. Results and discussions

3.1. Morphologies of microwave-treated graphite felt

The morphologies of the microwave-treated graphite felt were estimated based on the SEM photographs. Fig. 1 shows SEM images with the same magnification of original graphite felt (Fig. 1a), the sample graphite felt-30 h (Fig. 1b) and the following selected graphite felt with three different exposure times to microwave radiation: (1) graphite felt-10 min (Fig. 1c), (2) graphite felt-15 min (Fig. 1d), and (3) graphite felt-20 min (Fig. 1e). Based on the comparison, visible changes exist on the surface of graphite felt materials. There are some particles on the surface of the original graphite felt (Fig. 1a), due to the impurities adhering to the surface even after purification procedure, which can hinder the approach and adsorption of the vanadium ions and the electron transfer [16]. After the graphite felt treated by conventional thermal treatment or microwave treatment, the particles on the surface of graphite felt vanished. The graphite felt surface was etched and slightly rough

(Fig. 1b) after treated by thermal treatment for 30 h. When the graphite felt was treated by microwave for 10 min, the surface became more sculptured and rougher (Fig. 1c). With the exposure time of microwave radiation increasing further, the graphite felt fibers were etched like tree root as shown in Fig. 1d and e, whereas no visible change in the morphologies was detected between graphite felt-15 min (Fig. 1d) and graphite felt-20 min (Fig. 1e). Therefore, the rough degree of graphite felt increased after microwave treatment. These etches helped to increase a specific area to a great extent and improve the degrees of surface energy.

3.2. FT-IR for microwave-treated graphite felt

FT-IR was used to characterize the oxygen-containing groups in graphite felt fibers. Fig. 2 displays the FT-IR spectra of graphite felt samples. Some structural changes might have occurred during microwave treatment. The compared graphite felt-30 h is almost featureless, indicating the absence of functionalization. After microwave treatment, many bands have emerged, which indicate a

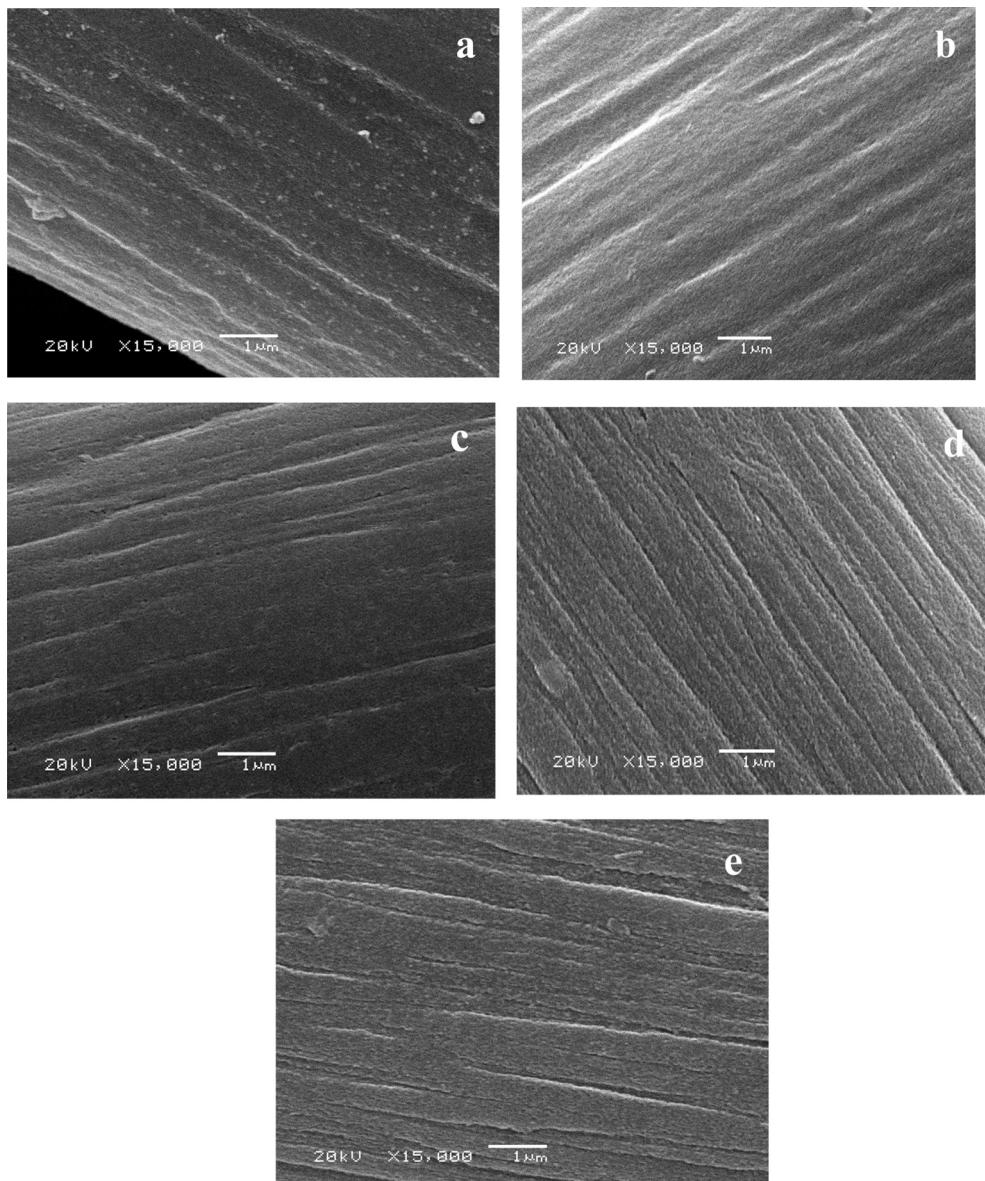


Fig. 1. SEM photographs of graphite felt. (a) Original graphite felt (b) graphite felt-30 h (c) graphite felt-10 min (d) graphite felt-15 min (e) graphite felt-20 min.

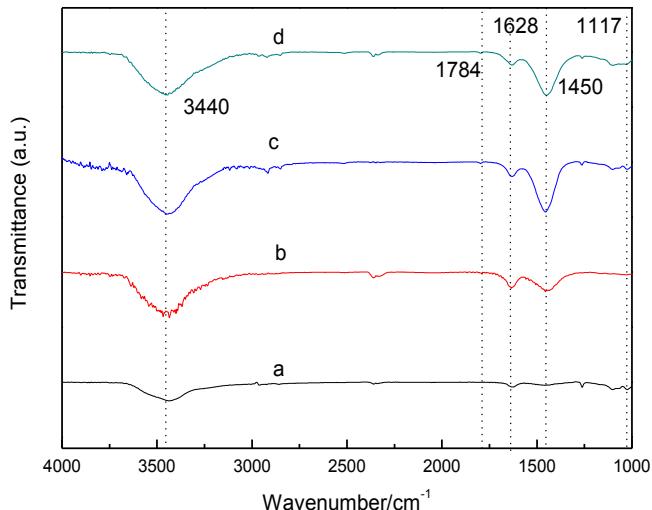


Fig. 2. FT-IR spectra of (a) graphite felt-30 h, (b) graphite felt-10 min, (c) graphite felt-15 min, and (d) graphite felt-20 min.

high degree of functionalization. The peaks at 3440 cm^{-1} and 1450 cm^{-1} were assigned to the O–H stretching and bending vibration. The peak at 1117 cm^{-1} was attributed to C–O stretching vibration [35]. The stretching mode of –OH groups in the enol (C=C–OH) appears at around 1628 cm^{-1} [36], and the peak at 1784 cm^{-1} was attributed to C=O groups in ketone, aldehyde, or lactone groups [37]. The intensity of the O–H stretching and bending vibration peak presented (3440 cm^{-1} , 1450 cm^{-1}) and –OH stretching vibration peak presented (1628 cm^{-1}) increases definitely in the graphite felt-15 min, indicating that the oxygen containing groups were successfully introduced to the surface of graphite felt fibers.

Moreover, the treated graphite felt-15 min carries more hydrophilic groups, such as –OH, on its defects, which should be favorable to electrochemical reaction. The increased –OH can provide more active sites and should be a vital precursor for electron transfer during the redox reaction of the V(IV)/V(V) couple [16,18].

3.3. Cyclic voltammetry and electrochemical impedance spectroscopy for microwave-treated graphite felt

To characterize the electrochemical activity of microwave-treated graphite felt electrodes for $\text{VO}^{2+}/\text{VO}_2^+$, the cyclic voltammograms of samples in $0.5\text{ M VOSO}_4 + 3\text{ M H}_2\text{SO}_4$ were measured. The CVs of graphite felt electrodes were compared and shown in Fig. 3. The oxidation and reduction peaks corresponding to a V(V)–V(IV) couple appear at approximately 1.2 V and 0.6 V(vs. SCE), respectively. The graphite felt-30 h has the lowest oxidation and reduction peak current density, which suggests that the untreated sample exhibited the worst electrochemical activity for $\text{VO}^{2+}/\text{VO}_2^+$ redox reaction. The oxidation peak current density exhibited a significant change with the duration time of microwave treatment. The peak currents of the oxidation and reduction of $\text{VO}^{2+} \rightleftharpoons \text{VO}_2^+$ on graphite felt-15 min are 119.4 and -82.04 mA cm^{-2} , respectively; the peak currents of the oxidation and reduction of $\text{VO}^{2+} \rightleftharpoons \text{VO}_2^+$ on graphite felt-30 h are 44.41 and -32.39 mA cm^{-2} , respectively. These results can be attributed to the formation of oxygen-containing groups on the surface of microwave-treated graphite felt and the rough degree of graphite felt. As a result of the improved hydrophilicity of the surface caused by the increased –OH group, the absorbed water on the graphite felt surface is increased, which may enhance the adsorption of vanadium ion on

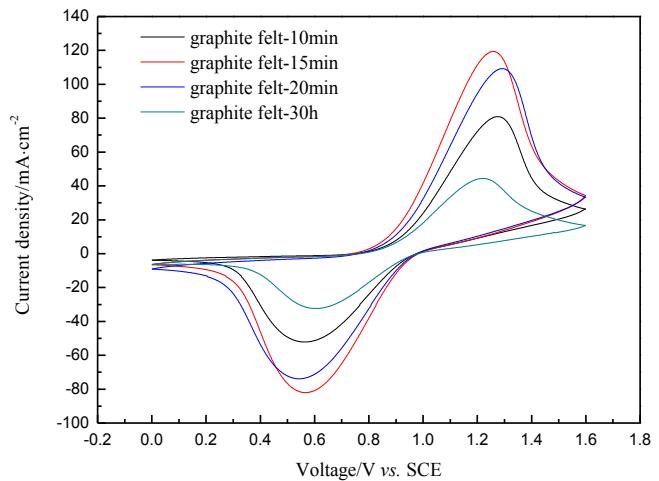


Fig. 3. Cyclic voltammograms of graphite felt treated by microwave and conventional thermal treatment.

the surface of electrode and benefit for electrode reaction. And those etches on the surface of graphite felt provided active sites for $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions which could help to increase electrocatalytic activity and reactive velocity to V(IV)/V(V) couple. Therefore, the coulomb efficiency of a VRFB that employs microwave-treated graphite felt-15 min can be significantly enhanced by boosting the chemical conversion of the electro-active species.

We carried out EIS measurement to further understand the electrode structure and charge transfer properties on the surface of resulting graphite felt electrode at several duration times of microwave treatment. The Nyquist complex-plane impedance plots of graphite felt are shown in Fig. 4. The plots exhibit a similar pattern: a depressed capacitive semi-circle in the high-frequency region and a sloping straight line in the low-frequency region. The inset in Fig. 4 shows the equivalent circuit derived from the Nyquist plots. The derived circuit was employed to quantitatively describe the change in impedance. R_s is bulk solution resistance, R_p is Faradaic interfacial charge-transfer resistance, CPE is the constant phase element that accounts for double-layer capacitance, and W is Warburg impedance. The bulk solution resistance of graphite felt treated with microwave and conventional thermal treatment has

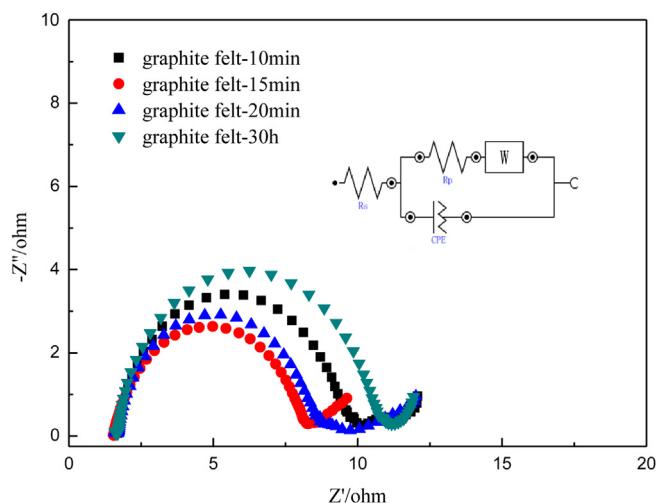


Fig. 4. Electrochemical impedance spectra of graphite felt treated by microwave and conventional thermal treatment.

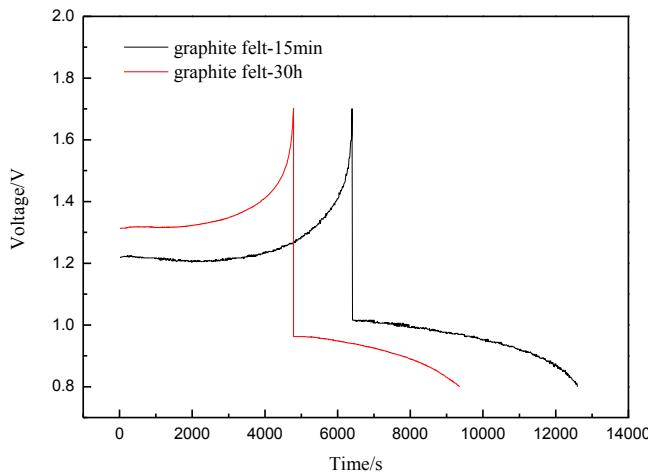


Fig. 5. Charge–discharge profiles of cells with graphite felt-15 min and graphite felt-30 h at a current density of 50 mA cm^{-2} .

similar values of 0.16Ω ; the corresponding charge-transfer resistance of graphite felt-15 min, graphite felt-30 h, graphite felt-10 min, and graphite felt-20 min is 6.55Ω , 9.12Ω , 8.24Ω , and 7.25Ω , respectively (deduced from the inset in Fig. 4). Therefore, the microwave-treated graphite felt-15 min causes charge-transfer resistance to decline, reflecting a higher reactive velocity, which corresponds to CV testing. This effect can be ascribed to the increase in $-\text{OH}$ groups on the electrode surface and the increase in the active site for the $\text{V(IV)}/\text{V(V)}$ redox reaction. Thus, the performance of VRFB is enhanced when the cell anode is treated by microwave for 15 min. The rules were in agreement with the changes of CV in Fig. 3.

3.4. VRFB single cell performance

Charge–discharge testing was conducted with a VRFB cell to further understand the effect of microwave-treated graphite felt-15 min. Fig. 5 presents the charge–discharge curves of two cells with graphite felt-15 min and graphite felt-30 h at a current density of 50 mA cm^{-2} . The curve of the cell with graphite felt-15 min as its electrode has a low and high discharge voltage plateau, thereby achieving extremely high voltage efficiency (VE) because the microwave treatment increased the ($\text{C}-\text{OH}$) groups. During charging, the oxidation of V(IV) to V(V) and oxygen evolution is competitive. The ($\text{C}-\text{OH}$) groups can catalyze the redox reaction of $\text{V(IV)}/\text{V(V)}$; as a result, the voltage and coulombic efficiency (CE) were improved, which is consistent with CV analysis. For the same reason, the cell with graphite felt-15 min exhibited high charge and discharge capacities. The detailed data obtained from Fig. 5 are summarized in Table 1. The VE and EE of the cell are 75.5% and 73.2% at a current density of 50 mA cm^{-2} , respectively.

The typical charge–discharge curves of the cell with graphite felt-15 min at current densities of 40 mA cm^{-2} , 50 mA cm^{-2} , 60 mA cm^{-2} , 70 mA cm^{-2} , and 80 mA cm^{-2} were tested and

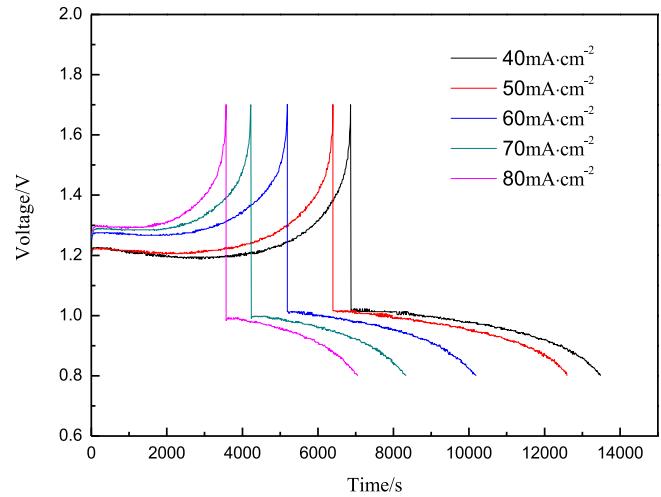


Fig. 6. Charge–discharge profiles of the cell with graphite felt-15 min at current densities of 40 mA cm^{-2} , 50 mA cm^{-2} , 60 mA cm^{-2} , 70 mA cm^{-2} , and 80 mA cm^{-2} .

Table 2

Efficiencies of the cell with graphite felt-15 min at current densities of 40 mA cm^{-2} , 50 mA cm^{-2} , 60 mA cm^{-2} , 70 mA cm^{-2} , and 80 mA cm^{-2} .

| Current density (mA cm^{-2}) | Coulombic efficiency (%) | Voltage efficiency (%) | Energy efficiency (%) |
|---|--------------------------|------------------------|-----------------------|
| 40 | 96.8 | 77.5 | 75.0 |
| 50 | 96.9 | 75.5 | 73.2 |
| 60 | 97.2 | 71.1 | 69.1 |
| 70 | 97.4 | 70.7 | 68.9 |
| 80 | 97.6 | 69.6 | 67.9 |

presented in Fig. 6. The cell maintained good charge–discharge performance at different current densities. The efficiencies of the cell are listed in Table 2. The CE, VE, and EE at 40 mA cm^{-2} are 96.8%, 77.5%, and 75.0%, respectively. The current density reached 80 mA cm^{-2} . VE remained higher than 69.6%.

Fig. 7 presents the EE data of the 50 charge–discharge cycles of the cell assembled with graphite felt-15 min at 50 mA cm^{-2} . No reduction in performance was observed; thus, the cell with the graphite felt-15 min has stable performance under the flowing electrolyte.

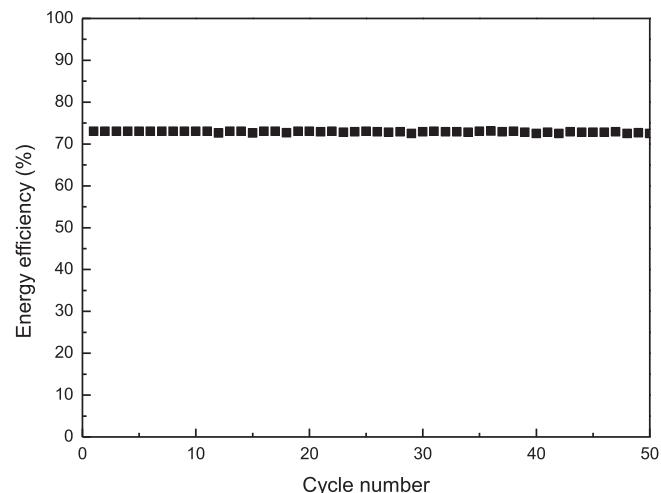


Fig. 7. Energy efficiency data of the 50 charge–discharge cycles of the cell with graphite felt-15 min at 50 mA cm^{-2} .

Table 1

Parameters obtained by fitting the charge and discharge curves in Fig. 5.

| Cells | Initial charge voltage (v) | Initial discharge voltage (v) | Voltage efficiency (%) | Charge capacity (mA h) | Discharge capacity (mA h) |
|---------------------------|----------------------------|-------------------------------|------------------------|-----------------------------------|--------------------------------------|
| With graphite felt-15 min | 1.22 | 1.02 | 75.5 | 1012.0 | 981.2 |
| With graphite felt-30 h | 1.31 | 0.96 | 72.3 | 797.7 | 746.2 |

4. Conclusions

Graphite felt electrodes treated by microwave were applied to a VRFB for the first time. The content of $-\text{OH}$ groups on the graphite felt fibers and the rough degree of graphite felt surface were increased by microwave treatment. As a result, the graphite felt treated with microwave for 15 min carries more hydrophilic groups, such as $-\text{OH}$, on its defects, which should be favorable to electrochemical reaction and those etches on the surface of graphite felt provided more active sites for $\text{VO}_2^+/\text{VO}_2^+$ redox reactions. The VRFB with the graphite felt treated by microwave for 15 min at 400 °C exhibits the best electrochemical activity for V(IV)/V(V) redox reaction. The CE, VE, and EE of the cell at a current density of 50 mA cm⁻² are 96.9%, 75.5%, and 73.2%, respectively; these values are much higher than those of the cell-assembled graphite felt prepared by conventional thermal treatment. No decrease in EE was observed after 50 charge–discharge cycles at 50 mA cm⁻². These results suggest that a simple surface treatment with microwave is a promising method for vanadium redox flow batteries in terms of production cost and electrochemical properties.

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